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(30) Priority Data (31) 08526895 (32) 12.09.1995 (33) US	(56) Documents Cited EP 0677883 A WO 84/02283 A US 3684712 A Abstracts of JP 04133328 A (Meidensha Corp.)
(71) Applicant(s) Electric Fuel (E.F.L.) Limited (Incorporated in Israel) 5 Kiryat Mada Street, Har Hotzvim Science Park, PO Box 23073, Jerusalem 91230, Israel	(58) Field of Search UK CL (Edition O) B2E EKB INT CL ⁶ B01D 53/14 53/62 Online: EDOC, JAPIO, WPI
(72) Inventor(s) Yehuda Harats Yuval Sharon Neal Naimer Jonathan Goldstein	
(74) Agent and/or Address for Service Boult Wade Tennant 27 Furnival Street, LONDON, EC4A 1PQ, United Kingdom	

(54) Coated absorbent particles for a carbon dioxide scrubber system

(57) The invention provides CO₂-absorbent particles for a CO₂ scrubber system comprising a plurality of pieces of substrate material, the pieces being coated with an at least partly enveloping outer layer formed of a CO₂ absorber, wherein the particles have a substantially inert core of substrate material and an average particle sizes in the range of about 6-14 mesh, and wherein the volume of the coating layer is about 20-40% of the substrate volume.

The substrate is preferably magnesium oxide granules and the absorber lithium hydroxide.

The scrubber system is used to remove carbon dioxide from air or fuel streams supplying metal-air or fuel cell batteries or respiratory breathing systems.

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IMPROVED CARBON DIOXIDE - ABSORBENT PARTICLES
FOR CARBON DIOXIDE SCRUBBER SYSTEM

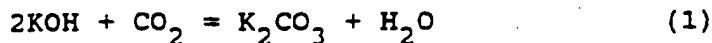
The present invention relates to CO_2 -absorbent particles for a scrubber system for removing carbon dioxide from air or fuel streams supplying a metal-air or fuel cell battery, or from respiratory breathing systems and to processes for the preparation thereof.

More particularly, the present invention relates to improved CO_2 absorbent particles for zinc-air battery scrubber systems of the type described in U.S. application 08/210,333 and corresponding EPC application 95301398.4, the teachings of which are incorporated herein by reference.

As is known, and as described, e.g., in U.S. Patent No. 3,909,206, alkali electrolyte fuel cells and metal-air batteries require a clean fuel and a clean oxidant to generate power. Many oxidants, such as air and all but the most pure, and therefore the most expensive, oxygen supplies and some fuels contain carbon dioxide (CO_2) which, when brought into contact with the electrolyte, combines with the electrolyte to form carbonates. The formation and presence of carbonates in the electrolyte decreases the voltage of the cells and batteries, and eventually causes their failure.

For this reason, a CO_2 scrubber system is applicable to a metal-air or fuel cell battery (e.g., zinc-air battery, hydrogen-air fuel cell) with an alkaline electrolyte (e.g., aqueous KOH) and incorporating an air electrode, supplied with air as the cathodic reactant. Regular air contains about 400 ppm of CO_2 , and if this CO_2 is not removed, the CO_2 can react with the KOH to form potassium carbonate

(K_2CO_3) , which will gradually build up in the alkaline electrolyte.



K_2CO_3 not only reduces the conductivity and alkalinity of the KOH, giving poorer cell polarization characteristics, but, being less soluble than KOH, can deposit carbonate crystals in the pores of the air electrode, especially in the presence of other sparingly soluble ions, such as zincates and aluminates in the electrolytes of zinc-air and aluminum-air cells respectively. These crystals can cause leaks and shorten the life of air electrodes.

In a related field, respiratory breathing systems in naval or aerospace units have CO_2 scrubbers which maintain the CO_2 concentration at a safe low level for breathing use.

The general absorption reaction of CO_2 by alkali metal hydroxide (MOH) may be written:



The prior art has therefore suggested the use of a scrubber system containing alkali hydroxide granules, held as a compact bed in a suitable container whose dimensions, the granule size, the granule loading and degree of packing of the granules are determined by such factors as the required air flow rate and flow time through to the battery, permitted pressure drop across the granule bed, permitted CO_2 exit concentration and degree of absorption required within the bed. Advantageously, the granules are retained between plastic screens somewhat finer than the granule

dimensions, and the scrubber system may be advantageously fitted with dust-retaining filters and/or moisture or droplet-retaining demisters. When the bed is no longer effective for scrubbing and CO_2 breakthrough occurs, as shown, for example, visually (by a color change of a chemical indicator impregnated on the granules, which signals chemical exhaustion of the bed) or electronically (by the output of a CO_2 detector, for example of the infra-red type, showing CO_2 levels above a certain predetermined value, for example, 50 ppm), the bed must be replaced.

There is therefore a need for a scrubber system of special application to serviceable batteries of the above type (e.g., mechanically-rechargeable zinc-air) or breathing equipment wherein there is a need to periodically maintain the CO_2 scrubber system, and it is desirable, for economical and/or ecological reasons, to reprocess the spent scrubber active material rather than simply disposing of spent scrubber material and using of fresh material.

U.S. Patent No. 3,909,206 teaches a scrubber using finely-ground alkali hydroxide particles mixed with fine particles of a hydrophobic material, such as polytetra-fluoroethylene, for removing carbon dioxide from a gas stream to a concentration of less than 0.25 ppm.

Although CO_2 levels may be reduced to less than 0.25 ppm, no means are provided for reprocessing the scrubber material, or for extending the effective life thereof.

U.S. Patent No. 3,990,912 for hydrogen-air fuel cells with alkaline electrolytes uses electrochemical means to convert K_2CO_3 in the cell electrolyte back to KOH, by means of an additional regenerator cell system with circulating

electrolyte that consumes hydrogen when it operates. This may be too complex, heavy and parasitic as to power needs for a mobile system application (e.g., an electric vehicle) and, requiring a source of hydrogen, will not be applicable to non-hydrogen systems (e.g., aluminum-air).

U.S. Patent No. 4,047,894 describes a scrubber element comprised of spaced-apart corrugated layers of porous PVC impregnated with CO₂-absorbing solution (e.g., 10 Moles/liter aqueous KOH). Although means for reuse of the element are described (column 3, lines 49-52), comprising rinsing with water, drying and reimpregnation with absorption solution, no means are given for reprocessing of the spent absorber to give fresh absorbent free of carbonate deposits, or for extending the effective life thereof by mechanical means.

As stated hereinbefore in co-pending U.S. application 08/210,333 and corresponding EPC application 95301398.4, the teachings of which are incorporated herein by reference, there is described and claimed a scrubber system for removing carbon dioxide from a metal-air or fuel cell battery. In said co-pending specification the CO₂ absorbent material used comprises a solution of Group 1a metal hydroxide in water absorbed into porous granules of an alkali-resistant material.

More particularly, the scrubber system described in said earlier co-pending specification was based on the use of a coarse, granular type CO₂-absorbent material (3-30 mesh), comprising an alkali metal hydroxide (e.g., selected from LiOH, NaOH, KOH). The hydroxide therein is described as being in the solid phase (either anhydrous or hydrated form), when advantageously a certain minimum porosity (50% minimum) of the granules will ensure some

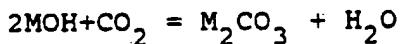
utilization of the inner portions of said granules. Alternatively, especially when the air to the scrubber/battery is prehumidified, the hydroxide may be in the form of an impregnated phase as an aqueous solution (e.g., 30-40 wt.% MOH) absorbed into porous carrier granules of an alkali-resistant plastic, ceramic or elastomer in foam, floc, chip or felt form. Examples of such materials are polyethylene, polypropylene, PVC, polystyrene, nylon, low-density brick, or rubber.

It has now been found that this approach is associated with a low utilization of the CO_2 absorbing material at the time of CO_2 breakthrough and that only the outer core of the granule, comprising typically 30-40% of the weight or volume of the active material, reacts.

This figure is very low and results in a large quantity of unreacted absorber having to be replaced or regenerated each time the scrubber is serviced. Unfortunately, the unreacted material is at the core of the granule, or absorbed within the substrate core, and no easy separation route exists. Some scrubber materials such as LiOH or its hydrate are preferred absorber materials for CO_2 because of the low weight ratio.

weight of absorbent taking up 1 mole CO_2
weight of 1 mole CO_2

associated with the CO_2 absorption reaction,



but these materials are expensive and their utilization should be increased.

With this state of the art in mind there is now provided, according to the present invention, CO_2 -absorbent particles

for a CO₂ scrubber system comprising a plurality of pieces of substrate material, said pieces being coated with an at least partly enveloping outer layer formed of a CO₂ absorber, wherein said particles have a substantially inert core of substrate material and an average particle size in the range of about 6-14 mesh, and wherein the volume of said coating layer is about 20-40% of the substrate volume.

In preferred embodiments of the present invention said substrated inert core substrate pieces have an average major axis of about 1-2 mm, and said coating has a thickness of about 100-500 microns.

In especially preferred embodiments of the present invention said substrate material is porous and has a porosity of at least 50% and a coarse pored structure with pore diameters in the range of 100-500 microns.

In another aspect of the present invention there is provided a process for the preparation of CO₂-absorbent particles for a CO₂ scrubber system comprising preparing porous pieces of substrate material, having a porosity of at least 50% and a coarse pored structure with pore diameters in the range of 100-500 microns, preparing a slurry of a CO₂ absorber material, placing said pieces of substrate material in a filtering container, and pouring said slurry over said pieces to form a coating layer on said pieces, followed by heating, wherein said formed particles have a substantially inert core of substrate material and an average particle size in the range of about 6-14 mesh, and wherein the volume of said coating layer is about 20-40% of the volume of the substrate pieces.

The invention also provides a process for the preparation of CO_2 -absorbent particles for a CO_2 scrubber system comprising preparing pieces of substrate material, preparing a slurry of a CO_2 absorber material or using the absorbent material directly and compressing said slurry or absorbent material onto the surface of said pieces of substrate material to form a coating layer on said pieces, wherein said formed particles having a substantially inert core of substrate material and an average particle size in the range of about 6-14 mesh, and wherein the volume of said coating layer is about 20-40% of the volume of the substrate pieces.

Thus, according to the present invention, there has now been developed a novel CO_2 absorbent material comprising porous granules of substrate, coated with CO_2 absorbent material. LiOH and its hydrate are preferred CO_2 absorbents of choice, though other Group Ia metal hydroxides may be used, and other CO_2 absorbers such as soda lime, sodium hydroxide with barium hydroxide, and amines. Similar to US Application 08/210,333 the substrate material may be porous pieces of an alkali resistant plastic, ceramic, carbon or elastomer in foam, floc, chip granule, or felt form. Examples of such materials are polyethylene, polypropylene, PVC, polystyrene, nylon, rubber, carbon and low density clay, rock or brick. However, in order for the coating of the absorber to adhere to the substrate granules (the absorbent material preferably being applied via the solid phase as a powder or a slurry onto the substrate granules, followed by heating as will be described below), there has been found that the substrate material should have a porosity of at least 50%, and a coarse pored structure with pore diameters in the range of 100-500 micron. Furthermore, the coated substrate, (which should have a particle size in the 6-14 mesh range for reasons discussed above), should conform to

an optimum volume distribution between the coating volume and the substrate volume, such that the coating volume is about 30% of the substrate volume. In practical terms for the aforementioned coated granule size of 6-14 mesh (2-4 mm diameter particles) the appropriate substrate diameter would be from 1-2 mm. At CO_2 breakthrough, the utilization of absorbent material may be doubled or trebled by means of this strategy.

A preferred substrate material for use in the present invention is magnesium oxide (MgO). The lithium hydroxide absorber, which is available (as raw material or from regeneration) as a fine powder whose particle size is in the 1-10 micron range, is first prepared as a 30 wt % slurry in a suitable carrier phase such as isopropyl alcohol or a saturated solution of 10 wt % lithium hydroxide in water. The magnesium oxide granules are placed into a filter funnel and are agitated gently by means of a plastic impeller. The lithium hydroxide slurry is then added into the filter funnel and the liquid phase continuously filtered off. The process is terminated when the apparent volume of lithium hydroxide corresponding to 30% the apparent volume of the magnesium oxide has been added and the liquid phase of the slurry has been substantially filtered off. The contents of the filter funnel are then turned out onto a plastic tray and heated at 50-150°C in a stream of CO₂ free air and/or subjected to vacuum. The coated granules may then be used as CO₂ scrubber material. Due to the viscous nature of the slurry liquid phase only a small quantity of dissolved LiOH enters the MgO granules. In a further embodiment, substrate pieces in fabricated form, for example plastic granules with one or more external cavities, can be loaded with absorbent slurry or absorbent powder by coating or compressing means into the cavity area, and then heated as above. Compression pressures range from 1-2 tons/cm².

While the invention will now be described in connection with certain preferred embodiments in the following examples so that aspects thereof may be more fully understood and appreciated, it is not intended to limit the invention to these particular embodiments. On the contrary, it is intended to cover all alternatives, modifications and equivalents as may be included within the scope of the invention as defined by the appended claims. Thus, the following examples which include preferred embodiments will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purposes of illustrative discussion of preferred embodiments of the present invention only and are presented in the cause of providing what is believed to be the most useful and readily understood description of formulation procedures as well as of the principles and conceptual aspects of the invention.

Example 1

Magnesium oxide substrate granules of porosity 70% and particle size 1-2mm were made by high temperature sintering of magnesium oxide powder (70 micron grade). Porosity measurements (Micrometrics) showed the predominant surface pores on the granules to be at least 150 microns in diameter. The CO₂ absorbent material taken to coat the magnesium oxide granules was lithium hydroxide powder (10-100 micron grade). A 50 gm sample of magnesium oxide granules was placed in a Buchner filter funnel and filter flask assembly fitted with a Whatman No. 41 filter paper and the granules could be agitated by means of a plastic impeller connected to an overhead stirrer. With the plastic impeller gently activated and the Buchner assembly connected to a water pump, a slurry comprising 30 gm of lithium hydroxide powder in a saturated solution of 70 gm of 10 wt%

lithium hydroxide in water was slowly poured over the magnesium oxide granules. After the liquid phase had been evacuated, the contents of the filter funnel were turned out onto a plastic tray and heated in a stream of CO_2 - free air at 55° for one hour. Inspection of the coated granules showed that the coating was quite firm and keyed in onto the coarse pored magnesium oxide cores and the mesh size of the coated granules fell in the 6-14 mesh range. By measuring the bulk volume of the substrate before and after coating it was shown that the coating comprised about 30% of the net substrate volume.

Example 2

The coated granules of Example 1 (30gm content lithium hydroxide) were compared as to scrubbing efficiency with an equivalent volume of 6-14 mesh commercial granules comprising only LiOH (50gm) by forcing regular air (400 ppm CO_2) at a flow rate of 150ml/minute over the packed granules in separate scrubber columns for two successive experiments until breakthrough occurred (>50 ppm CO_2 via an infra red CO_2 detector observed in the air exit stream). The coated material lasted about the same time till breakthrough as the commercial granules, showing a much higher utilization of available lithium hydroxide.

It will be evident to those skilled in the art that the invention is not limited to the details of the foregoing illustrative examples and that the present invention may be embodied in other specific forms without departing from the essential attributes thereof, and it is therefore desired that the present embodiments and examples be considered in all respects as illustrative and not restrictive, reference being made to the append d claims, rather than to the foregoing description, and all changes which come within the

meaning and range of equivalency of the claims are therefore intended to be embraced therein.

WHAT IS CLAIMED IS:

1. CO_2 -absorbent particles for a CO_2 scrubber system comprising a plurality of pieces of substrate material, said pieces being coated with an at least partly enveloping outer layer formed of a CO_2 absorber, wherein said particles have a substantially inert core of substrate material and an average particle size in the range of about 6-14 mesh, and wherein the volume of said coating layer is about 20-40% of the substrate volume.
2. CO_2 -absorbent particles according to claim 1, wherein said substrated inert core substrate pieces have an average major axis of about 1-2 mm, and wherein said coating has a thickness of about 100-500 microns.
3. CO_2 -absorbent particles according to claim 1, wherein said CO_2 absorber is selected from the group consisting of Group 1a metal hydroxides and hydrates thereof, soda lime, sodium hydroxide, barium hydroxide, amines and combinations thereof.
4. CO_2 -absorbent particles according to claim 1, wherein said CO_2 absorber is LiOH or a hydrate thereof.
5. CO_2 -absorbent particles according to claim 1, wherein said substrate pieces are formed of a material selected from the group consisting of alkali-resistant plastic, ceramic, carbon or elastomer in foam, floc, chip, granule, felt or fabricated carrier form.
6. CO_2 absorbent particles according to claim 5, wherein

the substrate pieces have at least one external cavity for receiving CO₂ absorbent material by coating or compressing means.

7. CO₂-absorbent particles according to claim 1, wherein said substrate material is selected from the group consisting of polyethylene, polypropylene, polyvinylchloride, polystyrene, nylon, rubber, carbon, and low density clay, rock and brick.

8. CO₂-absorbent particles according to claim 1, wherein the volume of said coating layer is 25-35% of the substrate volume.

9. CO₂-absorbent particles according to claim 1, wherein said substrate material is porous and has a porosity of at least 50% and a coarse pored structure with pore diameters in the range of 100-500 microns.

10. A process for the preparation of CO₂-absorbent particles for a CO₂ scrubber system comprising preparing porous pieces of substrate material, having a porosity of at least 50% and a coarse pored structure with pore diameters in the range of 100-500 microns, preparing a slurry of a CO₂ absorber material, placing said pieces of substrate material in a filtering container, pouring said slurry over said pieces to form a coating layer on said pieces, and heating the resultant particles, wherein said formed particles have a substantially inert core of substrate material and an average particle size in the range of about 6-14 mesh, and wherein the volume of said coating layer is about 20-40% of the volume of the substrate pieces.

11. A process for the preparation of CO₂-absorbent particles for a CO₂ scrubber system according to claim 10,

wherein said substrate material is magnesium oxide.

12. A process for the preparation of CO_2 -absorbent particles for a CO_2 scrubber system according to claim 10, wherein said CO_2 absorber is lithium hydroxide.

13. A process for the preparation of CO_2 -absorbent particles for a CO_2 scrubber system according to claim 10, wherein said pieces of substrate material are placed in a filtering apparatus and agitated gently by means of an impeller during the addition of said slurry thereto.

14. A process for the preparation of CO_2 -absorbent particles for a CO_2 scrubber system comprising preparing pieces of substrate material, preparing a slurry of a CO_2 absorber material or using solid absorbent material directly and compressing said slurry or absorbent material onto the surface of said pieces of substrate material to form a coating layer on said pieces, and heating the resultant particles, wherein said formed particles have a substantially inert core of substrate material and an average particle size in the range of about 6-14 mesh, and wherein the volume of said coating layer is about 20-40% of the volume of the substrate pieces.

15. CO_2 -absorbent particles for a CO_2 scrubber system as claimed in claim 1 substantially as hereinbefore described in Example 1.

16. A process for the preparation of CO_2 -absorbent particles as claimed in claim 10 substantially as hereinbefore described in Example 1.



Application No: GB 9618219.1
Claims searched: 1-16

Examiner: Diane Davies
Date of search: 11 December 1996

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): B2E: EKB

Int Cl (Ed.6): B01D 53/14, 53/62

Other: Online: CAS-ONLINE, EDOC, JAPIO, WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X.P	EP 0677883 A (Electric Fuel (EFL) Ltd.) Whole document: CO ₂ absorbent material for scrubber system of a battery or fuel cell impregnated on porous granules (see in particular column 5 lines 7-22).	1-16
X	WO 8402283 A (ICOR AB) Whole document: absorbent material having pellets (15) which are coated with a CO ₂ absorber.	1-16
X	US 3684712 A (A-T-O Inc.) Whole document: CO ₂ absorber comprising a composite of MgO particles and LiOH.	1-16
X	Abstract of JP 04133328 A (Meidansha Corp) CO ₂ absorber which is a zeolite coated with an azide.	1-16

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.